STUDIES IN HYDROTHERMAL ALTERATION

PART I. THE ACTION OF CERTAIN ALKALINE SOLUTIONS ON FELDSPARS AND HORNBLENDE

E. A. STEPHENSON
University of Chicago

In the study of ore deposits from a genetic standpoint the subject of attendant wall-rock alteration has received deserved attention from geologists. Profound changes of a chemical and mineralogical character have been recorded at many places, and the relation existing between the various types of wall-rock alteration accompanying ore deposition led to the suggestion that a knowledge of the conditions which bring about such alteration would throw great light on the problem of ore genesis. The data obtained in regard to the temperatures, pressures, and nature of solutions would also be of value in interpreting the geologic history of such occurrences.

The most important of these alteration minerals are kaolin, sericite, and chlorite, and the knowledge concerning their origin is chiefly confined at present to speculations based on their modes of occurrence and their associated minerals. There is especially great difference of opinion[1] as to the origin of kaolin. By some writers kaolinitic alteration is attributed to the action of meteoric waters rich in carbonic acid, by others to meteoric waters which have made a cycle of underground courses, and by still others to the emanations from a cooling magma while these are possibly yet in a gaseous state. In regard to sericite and chlorite associated with ore bodies there is nearly general agreement that these have been formed by the action of the solutions which deposited the primary minerals, whether these solutions be magmatic or meteoric, upon the feld-

[1] Bibliographies of the literature on kaolin are given by Rösler, *Neues Jahrb.*, Beil. Bd. XV (1902), 231, and by Lazarevic, *Zeit. prakt. Geol.*, XXI (1913), 345. An introduction to a discussion of the origin of kaolin was initiated by Lindgren, *Econ. Geol.*, January, 1915.

spars and the ferromagnesian minerals. Calcite and quartz are also prominent products of these reactions. Further, the relations of these minerals to the ores indicate that the processes of alteration and ore deposition have gone on contemporaneously. This is shown by the progressive decrease in the intensity of the alteration laterally from the veins, and by changes in the character of the alteration in the same direction. For example, the following extract from the report by F. L. Ransome[1] on the "Economic Geology of the Silverton Quadrangle" illustrates these points.

At points 150 feet east of the lode the country rock is fine-grained and faintly mottled, showing only a few pale phenocrysts of feldspar and an occasional tiny grain of quartz. Under the microscope the rock reveals the character of a much-altered andesitic tuff or fine breccia. The feldspars have been completely altered to aggregates of sericite and calcite, while areas of calcite and chlorite probably represent former phenocrysts of augite. The groundmass is a rather indistinct aggregate of secondary quartz, sericite, and chlorite with a little apatite and rutile. The rock is wholly recrystallized into a secondary aggregate while retaining the gross structure of the original.

At a distance of 100 feet from the vein the . . . . chlorite and calcite are abundant, but much of the plagioclase is still recognizable. Sericite and quartz are not such prominent constituents. . . . .

At 50 feet from the vein . . . . the feldspar phenocrysts have been changed to aggregates of calcite and sericite, while areas of chlorite and calcite with sometimes rutile are all that remain of the phenocrysts of augite or biotite. The groundmass also, while preserving the outlines and in small part the substance of former lath-shaped feldspars, is now an aggregate consisting chiefly of quartz, chlorite, sericite, and a little rutile and apatite. . . . .

At 2 feet from the vein . . . . it is seen that alteration has been more thorough. . . . . The forms of the phenocrysts are preserved by pseudomorphous aggregates of sericite with some chlorite, calcite, and rutile apparently after biotite, and quartz, sericite, and chlorite in varying proportions after augite and plagioclase. The groundmass is entirely recrystallized . . . . and the dominant minerals are quartz and sericite.

A specimen taken from the wall of the vein showed more evident alteration . . . . and the rock is wholly recrystallized. The former phenocrysts of feldspar are replaced by pseudomorphus aggregates of quartz and sericite. . . . . Of the augite no trace remains, but some sericite inclosing rutile is apparently pseudomorphous after biotite. The groundmass is a finely crystalline mosaic of quartz and sericite. The notable feature of this wall rock is the absence of calcite and chlorite. . . . .

[1] F. L. Ransome, *Bull. 182*, *U.S. Geol. Survey*, pp. 116–18.

To sum up then, the alteration involves the change of the feldspars to sericite, calcite, and quartz; of augite to calcite and chlorite; and of biotite to chlorite, sericite, and rutile.

Chloritic alteration appears to precede sericitic alteration and to require less intense or less prolonged action or solutions of a different character, so that sericite is found closer to the veins than chlorite, and chlorite dominates farther from the veins. It may be in place here to note that many consider the solutions which emanate from the magma in its final stages acidic in character while others hold that they are alkaline. A study of volcanic gases and of the sublimates present in craters indicates that the volcanic vapors are quite certainly acid, and Day and Shepherd[1] found that the magmatic waters which they collected from the small dome within the crater at Kilauea were acid. However, to conceive of these solutions as remaining acid for a long journey through rock masses after their escape from the magma requires a high degree of acidity, and geologists have been loath to accept such a view.

It is clear then that the experimental formation of these alteration products from the feldspars and ferromagnesian minerals will give some clew as to the nature of the solutions and the temperature and pressure conditions that obtained during the deposition of the associated primary ore bodies. A study of the literature bearing on the subject of the hydrothermal alteration and syntheses of various silicates leaves the reader somewhat at a loss to discern the geologic application of much of the data. Some of the experimental work is of great interest chemically but not geologically. Hydrothermal investigations that begin with mixtures of oxides instead of with distinct mineral species may have in many cases comparatively little geologic significance. When the definite mineral can be prepared synthetically from pure materials, nearly ideal conditions may be obtained, with results that are beyond question. However, since many of the minerals whose investigation is of paramount interest and importance in their relation to the analysis of geologic processes cannot be prepared synthetically, the next

[1] A. L. Day and E. S. Shepherd, *Bull. Geol. Soc. Am.*, XXIV, 593.

[2] This literature is ably reviewed by G. W. Morey and Paul Niggli in *Jour. Am. Chem. Soc.*, XXXV, No. 9 (September, 1913), 1106-30.

best course to adopt is to use minerals of as high degree of purity as are available. The fusion of such a mineral before its investigation must be vigorously condemned because it is well established that the minerals which crystallize from a melt are not always like those which were originally fused, and in many cases several distinct minerals are produced by this process from a single species. If the glass that is formed by the fusion is used, it may differ chemically from the original mineral by the loss of volatile gases, and it must differ in its energy content.

For example, Lemberg's[1] important work is in part open to these criticisms, though the volume of data supplied by him is remarkable. Other work of this sort has been carried on in glass containers which of themselves may have furnished a most important source of error. Further, the concentrations of the solutions which have been used, as a rule, have been far in excess of those known to exist in ground or hot spring waters. Just how much difference this would make in the results obtained is not yet clear, though it is highly probable that the solutions as they come direct from the magma are far more concentrated than those which appear at the surface in the form of hot springs. It is also recognized that such solutions, after having been in contact with the wall rock throughout their courses, have probably changed notably their compositions and concentrations and may bear but small traces of some of their original constituents. As a result of these considerations it is at present an open question how much geologic significance is to be attached to investigations carried on with such concentrations as Lemberg used, though his results have thrown much light on methods of attacking the problem of mineral alteration. Other investigators, especially Thugutt,[2] Königsberger and Müller,[3] Friedel and Grandjean,[4] Baur,[5] and Chroustschoff,[6] have contributed highly suggestive data.

[1] J. Lemberg, *Zeit. deut. geo.. Ges.*, Vols. XXXV, XXXVII, XXXIX, LX.

[2] J. S. Thugutt, *Zeit. anorg. Chem.*, II, 64–107, 113–16; *Neues Jahrb. Min. Geol.*, Beil. Bd. IX, 554–624.

[3] Königsberger and Müller, *Centralbl. Min.*, 1906, pp. 339–48, 353–72.

[4] Friedel and Grandjean, *Bull. Soc. Min.*, XXXII, 150–54.

[5] Emil Baur, *Zeit. physik. Chem.*, LXI, 567–76; *Zeit. anorg. Chem.*, LXXII, 119–61.

[6] K. von Chroustschoff, *Compt. Rend.*, CXII, 677–79.

At the suggestion of Professor W. H. Emmons, the writer began in 1912 a series of investigations of a hydrothermal character with particular reference to the geologic application of the results. It was hoped to contribute something concerning the temperatures, pressures, nature, and concentrations of the solutions which produce new materials from the feldspars and from some of the ferromagnesian minerals.

PLAN OF THE WORK

The plan of the work has been to try the effect of various simple dilute solutions upon the feldspars and one ferromagnesian mineral at various temperatures and pressures. This has been done up to 280° C., at intervals of about 50°. It is planned to work on up to about 500° C. if the results justify such a course. The solutions have been tried at various concentrations, for different lengths of time, besides the different temperatures.

The minerals used have been nearly pure species. A high-grade adularia from the St. Gotthard tunnel, albite from the Amelia Court House locality, orthoclase from Elam, Delaware County, Pennsylvania, microcline from C. A. F. Kahlbaum (locality not known), and an aluminous hornblende from Renfrew, Ontario, Canada. These have in all cases been powdered to pass a 100-mesh sieve, and portions exactly or approximately one gram in weight have been used for each experiment.

THE OVEN

For work at temperatures above 100° C., the oven described as follows was constructed (Fig. 1). A box $28\frac{1}{2} \times 15 \times 16$ inches (outside measurements), made of sheet iron, is fastened at the edges to a similar box $26\frac{1}{2} \times 13 \times 15$ inches placed inside of it, with the space between packed with asbestos. A door at the front extends the full length and height of the oven, opening outward with hinges along the bottom. Two holes are cut in the top at H and H', Fig. 2, for the insertion of thermometers. A number of holes, o and o', about $1\frac{1}{2}$ inches in diameter are also cut in one end of the box, Fig. 3. When the oven is in use these holes are closed with loosely packed asbestos wool.

The heating arrangement consists of six coils of No. 22 nichrome wire wound on asbestos boards $\frac{1}{2}$ inch thick, 1 inch high, and 7 inches long. Each coil has a carrying capacity of three amperes and is securely fastened to the bottom in order that the box may be used in any position. Three of these coils are connected to a three-way snap switch A, and three with a similar switch A', Fig. 4. By this means from three to eighteen amperes may be in use at one
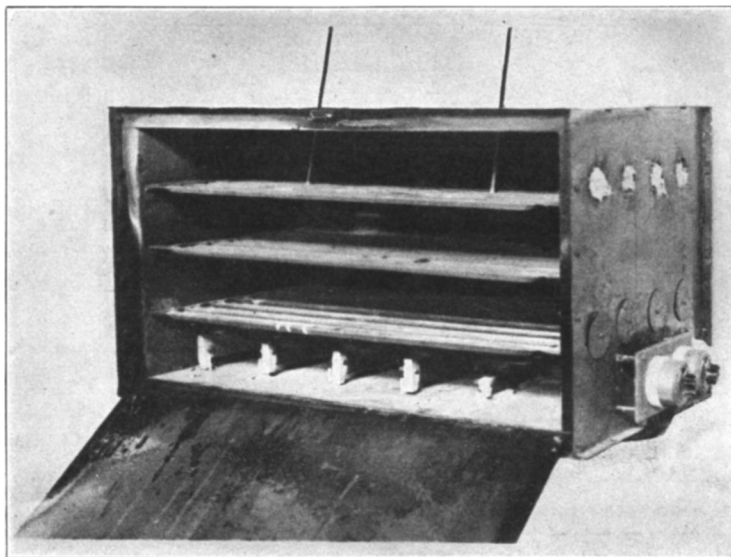
FIG. 1.—A view of the oven

time. The return wire is L, Fig. 4, which is also grounded on the box. The connections of coils Nos. 3 and 5, Fig. 4, pass to the thermo-regulator, T, Fig. 2, at R and R', thence through the screws K and K', Fig. 5, to the platinum contacts Pt, through the strip S to the box and out via the lead wire L to B, the socket, Fig. 4.

The construction of the thermo-regulator is as follows. A strip S, consisting of an above piece of copper 0.022 inch thick, is brazed to a piece of steel of the same thickness, and split longitudinally for an inch back from the free end so as to produce two contacts. S, Fig. 6, is fastened to the under side of block B, Fig. 5, which is pivoted between E and E'. The latter are inset along the

sides of the base plate A. D is a brass rod brazed to the block B, making D–B–S a continuous piece pivoted at V, Fig. 6. S', Fig. 6, is a steel spring pressing firmly against the under side of D so that
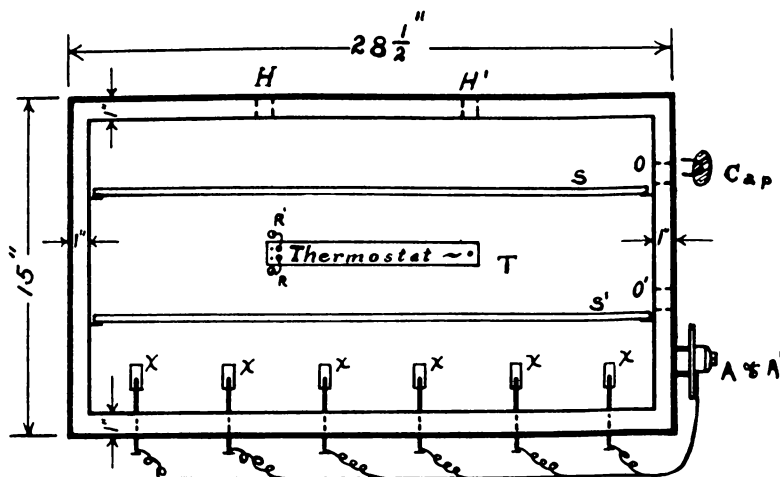
FIG. 2.—Front elevation of the oven

it is held close to the tip of screw C even when the contacts Pt are broken. M and M' are mica strips insulating R and R' from the rest of the device. W is a copper washer. H, Fig. 6, represents holes in the base plate A, through which bolts pass that hold the regulator against the back of the oven. A small condenser, not shown, is shunted around K and Pt, Fig. 6.
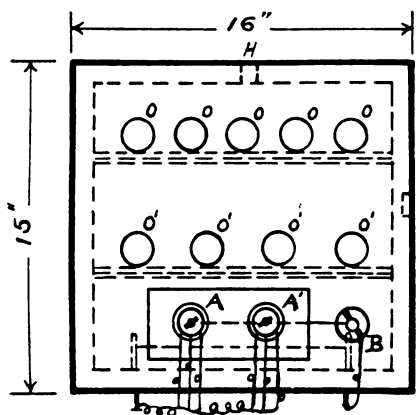
FIG. 3.—End elevation of the oven

Since the temperature coefficient of copper is greater than that of steel, a rise in temperature causes the strip S to bend the contacts Pt away from the tips of the screws K and K', and thus cut out the coils Nos. 3 and 5. The fall of temperature which results causes a reversal of the bend of the strip until the contacts are again made

at *Pt*, and the temperature rises. To adjust the oven for operation at higher or lower temperatures the screw *C*, Fig. 6, is turned in and the oven allowed to come to constant temperature. This requires about one hour. If the temperature so obtained is too low, the screw must be turned in still farther and such adjustments continued until the desired point is reached. Since the sensitiveness of the oven is much greater with both contacts acting together, and the expansion of the metals produces some torsion, it is necessary to adjust the screws at *K* and *K'*, until both coils Nos. 3 and 5
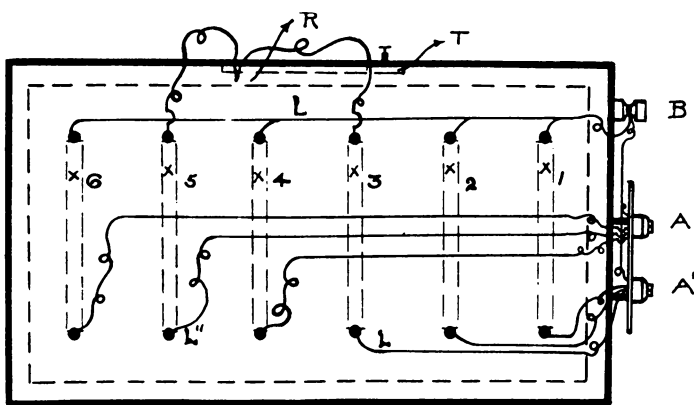
FIG. 4.—Under side of oven, showing wiring and arrangement of coils

come on or off together. Parts of the regulator not otherwise described are made of brass.[1]

This oven has proved highly satisfactory when used on an ordinary 110-volt power or lighting circuit. At the highest temperature at which it has been used, 300° C., the variations during several weeks have not been more than 3°. It has been in use as long as three months continuously, with similar slight variation, at about 180° C. Greater sensitiveness can be obtained by lengthening the strip *S*. The device has also served as an efficient drying oven. When but one of the six coils is being used—preferably No. 4, because it is centrally placed—it maintains a temperature averaging around 110° C., without having the regulator in the circuit.

[1] The writer is indebted to Captain A. De Khotinsky of Kent Chemical Laboratory for the greater part of the work in the design and construction of the oven.

In the early part of the investigation Jena glass tubes were used, provided with an inner tube of copper open at one end, in which the minerals and solutions were placed. This prevented contact of the solutions and the glass when the apparatus was placed in a nearly vertical position, but left only a small part of the solutions in direct contact with the mineral powder. Where glass tubes were used, these were first placed inside of steel tubes made of ordinary steam pipe $1\frac{1}{2}$ inches inside diameter, closed at one end by a screw
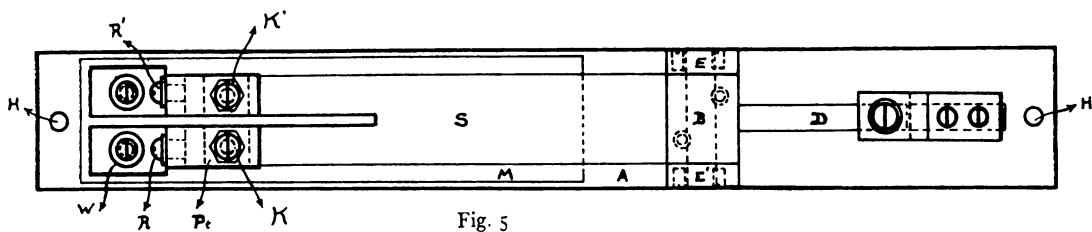
Fig. 5
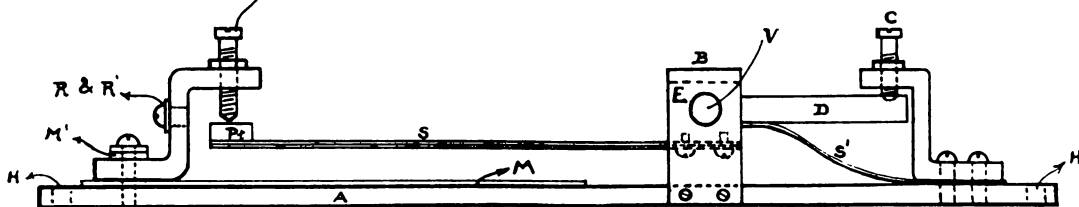
Fig. 6

FIG. 5.—Thermo-regulator, plan.   FIG. 6.—Thermo-regulator, side elevation

cap and placed in the oven with the open end against one of the holes o and o', Fig. 3.   Accidents to the thermo-regulator from possible explosions were thus prevented, though the trouble caused by bursting of the glass tubes led to their abandonment.   In their place copper tubes about 18 to 22 inches long with $\frac{5}{8}$ inch inside diameter and $\frac{1}{16}$-inch walls were used.   One end of each of these was closed with a plug of copper about $\frac{1}{8}$ inch thick driven in about $\frac{1}{8}$ inch past the end of the tube and the end then sealed in an oxy-acetylene flame.   The solution and the mineral powder were then placed in the tube, a plug of copper inserted as above, and the end then sealed while the tube was partly immersed in a freezing mixture.

These tubes have a calculated bursting strength of 6,000 pounds to the square inch and have proved highly satisfactory. They have been practically unattacked except by sulphide solutions, in which cases the tubes were found lined with beautiful chalcocite crystals.[1] They cost after sealing about one-half as much as Jena bombs of similar size and can be used repeatedly. The oven will accommodate about fifty such tubes at one time.

EXPERIMENTAL WORK

Group I: Effect of pure water on feldspar and hornblende.—In many hydrothermal processes it is not yet clear how significant a rôle is played by the water independent of the dissolved matter. Hence the first step in this investigation was an attempt to determine the efficiency of pure water in such processes. Accordingly the powdered minerals were covered with 300 c.c. of distilled water in open nickel crucibles with a device for maintaining the water at constant volume. The crucibles were placed on electric hot plates

TABLE I

No.	Mineral	Time	Vol. of Solution	Vol. Tube	Temp.	Press. Atm.	Results
1......	Adularia	14 days	300 c.c.	....	100° C.	1	No alkalinity
2......	Hornblende	14	300	....	100°	1	" "
3......	Adularia	82	50	80 c.c.	183°	11	" "
4......	Hornblende	82	50	80	183°	11	" "

and the water kept boiling for 14 days. At the end of that time the solutions were tested for alkalinity with neutral litmus paper and phenolphthalein. No change of color appeared after five minutes' standing. A similar pair of experiments at 180° C. in the sealed copper tubes ran for 82 days and at the end of that time the solutions were similarly tested and again no alkalinity developed. The minerals were then examined under the microscope and compared with slides of untreated mineral (Table I). No change could be detected. These results are not quite in accord with those of

[1] In certain cases a small amount of copper recrystallized on the plugs, probably owing to the fact that the drawn copper has a higher solution tension than crystalline copper.

Clarke[1] and Steiger,[2] who found that the solutions obtained by allowing various minerals—including orthoclase—and rocks to stand in contact with water containing a few drops of phenolphthalein developed more or less alkalinity. Cornu[3] obtained an alkaline reaction toward moist litmus paper from various powdered minerals. Königsberger and Müller[4] found also that adularia was but little attacked at 300° C. by pure water, the chief attack being parallel to the principal cleavage. Up to this temperature water alone is not to be considered an important reagent toward adularia or hornblende.

Group II: Effect of sodium carbonate solutions on feldspars.— The efficiency of carbonate solutions in hydrothermal processes is commonly conceded; this conclusion is based on the abundance of carbon dioxide in certain hot spring waters, and the presence of carbonates in the altered rocks and in the veins. The data given by Clarke[5] and by Peale[6] show not only that carbon dioxide dominates

TABLE II

No.	Mineral	Time	Solution	Concentration	Vol. Sol.	Vol. Tube	Temp.	Press. Atm.	Results
5..	Adularia	3 yrs. 1 mo.	Na_2CO_3	N/2	1,000 c.c.	......	15° C. *ca.*	1	No change
6..	"	90 days	"	"	300	......	100° C.	1	" "
7..	"	82	"	"	50	80 c.c.	183°	11	Analcite
8..	"	18	"	"	40	85	233°	30	"
9..	Microcline	18	"	"	40	75	233°	30	"
10..	Albite	18	"	"	40	85	233°	30	{Tube { burst

in certain thermal waters but that sodium is generally an abundant metallic ion in such waters. The concentration is low, rarely reaching as much as 1 per cent, though the carbonates make up as much as or even more than three-fourths of the total dissolved matter. In order then to follow the original plan and to use solutions comparable to those found in nature, solutions of sodium carbonate were employed as shown in Table II. The concentration

[1] F. W. Clarke, *Jour. Am. Chem. Soc.*, XX, 739–42.
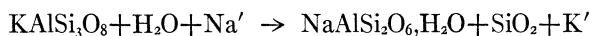
[2] George Steiger, *ibid.*, XXI, 437–39.

[3] F. Cornu, *Tschermak's Mitteilungen*, XXIV, 417–32.   [4] *Op. cit.*, p. 360.

[5] F. W. Clarke, *Bull. 491, U.S. Geol. Survey*, pp. 180–81.

[6] A. C. Peale, *Bull. 32, U.S. Geol. Survey*.

of one-half normal is equivalent to nearly 2.8 per cent. The minerals in Nos. 5 and 6 showed no change under the microscope. Tube No. 10 burst owing to defective sealing, but the mineral was unchanged. In all the others crystals of analcite formed along the sides of the tubes and around grains of feldspar as nuclei. Solution No. 6 was not saved, but the solutions from Nos. 7, 8, and 9 were placed in paraffin-lined bottles and on examination after several weeks' standing showed heavy gelatinous precipitates. These precipitates were then examined and were found to consist of silica and water. In spite of the fact that tube No. 10 burst, the results obtained from later experiments, notably Nos. 33 and 34, make it certain that similar results would have been secured had no accident occurred.

These facts indicate definite attack and solution of the feldspars with loss of one molecule of silica from each molecule of feldspar together with an exchange of the potash of the adularia for the soda of the solution. The following equations, using empirical formulae, indicate the reactions, which have positive experimental basis.

$$KAlSi_3O_8 + H_2O + Na' \rightarrow NaAlSi_2O_6, H_2O + SiO_2 + K'$$

and

$$NaAlSi_3O_8 + H_2O + Na' \rightarrow NaAlSi_2O_6, H_2O + SiO_2 + Na'.$$

The analcite was identified optically and also by sifting out the unchanged feldspar with its adhering analcite, gelatinizing the remaining crystals with hydrochloric acid, and allowing a small portion of the solution to crystallize out under the microscope as sodium chloride; the remaining portion of the solution was tested for alumina with ammonia water. After drying at 110° C., the crystals yielded water in a closed tube.

Group III: Sodium carbonate solutions on hornblende.—A series of experiments, Nos. 11, 12, and 13, exactly like those in Group II, were then tried with hornblende as the mineral (Table III). In no

TABLE III

No.	Mineral	Time	Solution	Concentration	Vol. Sol.	Vol. Tube	Temp.	Press. Atm.	Results
11..	Hornblende	3 yrs. 1 mo.	Na₂CO₃	N/2	1,200 c.c.	......	15° C. *ca.*	1	No change
12..	"	90 days	"	"	300	......	100° C.	1	" "
13..	"	82	"	"	60	85 c.c.	183°	11	" "

case did there appear, under the microscope, to be any change. No gelatinous silica separated from the solutions after long standing.

Group IV: Potassium fluoride solutions on feldspars and horn-blende.—Fluorine has long been looked upon as one of nature's important mineralizers;[1] it occurs in small quantities in the emanations from Kilauea,[2] is abundant as fluorite in metalliferous veins, is a constituent of many minerals such as apatite, amblygonite, lepidolite, topaz, and cryolite, and is considered by Spurr[3] an essential constituent of muscovite. Table IV shows the experiments con-

TABLE IV

No.	Mineral	Time	Solution	Concentration	Vol. Sol.	Vol. Tube	Temp.	Press. Atm.	Results
14..	Adularia	82 days	KF*	N/10	60 c.c.	85 c.c.	183° C.	11	No change
15..	"	18	"	"	50	80	233°	30	" "
16..	Microcline	18	"	"	40	75	233°	30	Minute rods
17..	Albite	18	"	"	30	70	233°	30	No change
18..	Hornblende	82	"	"	60	85	183°	11	Brown iron oxide
19..	"	15	"	"	50	75	233°	30	Tube burst

*This salt contained a small amount of the acid salt HKF₂.

ducted with potassium fluoride. In experiments Nos. 14, 15, 16, and 17 the feldspars showed no change other than a possible slight etching. In No. 16 there appeared some minute bacteria-like rods that were not further identifiable. In No. 18 the hornblende was vigorously attacked. The product is an amorphous brown mass resembling limonite and consisting of hydrated iron oxide together with grains of partially altered mineral. Some of these grains are bleached to isotropic transparency, others have a rim of isotropic matter surrounding ellipsoidal grains in the interior. No gelatinous precipitate appeared in the decanted solution on standing in paraffin lined bottles for several months. In No. 19 the tube burst and the mineral appeared unchanged.

Group V: Mixtures of carbonate and fluoride solutions on feldspars and hornblende.—Since the feldspars were not visibly attacked by the fluoride solutions but had been attacked by the alkaline carbo-

[1] See especially C. Doelter, *Allgem. chem. Min.*, p. 207, and W. Bruhns, *Neues Jahrb. Min. Geol.*, II (1889), p. 26.

[2] A. L. Day and E. S. Shepherd, *Bull. Geol. Soc. Am.*, XXIV, 592.

[3] J. E. Spurr, *Professional Paper 42, U.S. Geol. Survey*, p. 233.

nate solutions, it was deemed advisable to try a mixture of the two solutions to see if the traces of fluoride present would modify the results in any way (Table V). The feldspars in Nos. 20, 21, and 22

TABLE V

No.	Mineral	Time	Solution	Concentration	Vol. Sol.	Vol. Tube	Temp.	Press. Atm.	Results
20..	Adularia	90 days	Na$_2$CO$_3$+KF	N/2+N/10	300c.c.	......	100° C.	1	No change
21..	"	41	" "	" "	54	80c.c.	183°	11	" "
22..	"	82	" "	" "	60	80	183°	11	" "
23..	"	18	" "	" "	40	85	233°	30	Analcite
24..	"	15	" "	" "	60	100	280°	65	Needles
25..	Orthoclase	15	" "	" "	50	100	280°	65	Twins of unknown mineral, also needles
26..	Microcline	18	" "	" "	48	100	233°	30	No positive change
27..	Albite	18	" "	" "	48	80	233°	30	Analcite
28..	Hornblende	90	" "	" "	300	......	100°	1	No change
29..	"	41	" "	" "	60	85	183°	11	" "
30..	"	82	" "	" "	60	85	183°	11	" "
31..	"	3	" "	" "	60	85	233°	30	" "

were not visibly attacked and the decanted solutions gave no precipitate on standing. No. 23 showed crystals of analcite. No. 24 showed some needles with parallel, or nearly parallel, extinction and possibly some isotropic forms, though these were not positively identified. No. 25 contained many needles like those in No. 24 with no analcite. These needles have an extinction angle of less than 2°; index in the direction of elongation is 1.490, and at right angles to this 1.517; elongation is negative. The crystals after drying at 110° C. yield no water in a closed tube. Good terminations at both ends are common. No. 25 also

FIG. 7.—Twinned crystals produced by experiment No. 25.

contained beautifully twinned crystals, illustrated in the accompanying sketch (Fig. 7) made with a camera lucida. The crystals
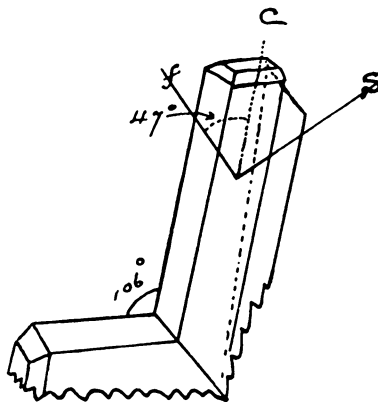
are perfectly transparent, have an index close to but greater than
1.565, an extinction angle of 43°, and are probably monoclinic. In
experiment No. 26 no evidence of any change appeared. In experi-
ment No. 27 icositetrahedra of analcite appeared, some free and
some including fragments of the feldspar. The hornblende in all
of this group of experiments was unchanged. It is concluded that
the presence of the fluoride had practically no influence upon the
alteration.

*Group VI: Sodium bicarbonate solution upon feldspars and
hornblende.*—These experiments embody an attempt to increase the
pressure both by raising the temperature and by increasing the
concentration of the carbon dioxide through dissociation of bicar-
bonates (Table VI). In experiment No. 32 scarcely any feldspar

TABLE VI

No.	Mineral	Time	Solution	Concen-tration	Vol. Sol.	Vol. Tube	Temp.	Press. Atm.	Results
32..	Adularia	15 days	NaHCO₃	N/2	45 c.c.	85 c.c.	233° C.	30	Analcite
33..	"	15	"	"	50	85	280°	65	"
34..	Albite	15	"	"	45	85	233°	30	Analcite and needles
35..	"	15	"	"	60	105	280°	65	Tube burst, but needles forme
36..	Hornblende	15	"	"	45	85	233°	30	No change
37..	"	15	"	"	45	85	280°	65	" "

remained and much analcite appeared as free crystals and as aggre-
gates. Gelatinous silica appeared in the decanted solutions after
some time. Similar results with decided etching of the feldspar
grains appeared in No. 33 where the pressure was practically
doubled. Possibly less analcite formed in this than in the previous
experiment at the lower temperature. In No. 34 with albite, anal-
cite also formed with many needles like those in experiment No. 25,
Table V. In experiment No. 35 the tube burst where poorly sealed,
but the mineral was nearly all altered to needles as in experiments
Nos. 24, 25 and 34. These were analyzed qualitatively and found to
consist of soda, alumina, and silica and yielded no water in a closed
tube. The writer was not able to find any natural sodium alumi-
num silicate whose properties agree with these. Needles having

the same optical properties as these also appeared in experiment No. 46 and are undoubtedly the same thing.

The hornblende was unchanged in experiments No. 36 and 37; the tube in No. 37 burst some time during the course of the heating.

Group VII: Potassium bicarbonate solutions on feldspars and hornblende.—These are similar to the experiments of Group VI, except that potassium bicarbonate solutions were substituted for the sodium bicarbonate solutions (Table VII). In no case either

TABLE VII

No.	Mineral	Time	Solution	Concentration	Vol. Sol.	Vol. Tube	Temp.	Press. Atm.	Results
38..	Adularia	15 days	KHCO$_3$	N/2	45 c.c.	75 c.c.	233° C.	30	No change
39..	"	15	"	"	50	90	280°	65	" "
40..	Albite	15	"	"	45	75	233°	30	" "
41..	"	15	"	"	60	105	280°	65	" "
42..	Hornblende	15	"	"	45	100	233°	30	" "

with the soda or potash feldspar or with hornblende did any change appear in the minerals. The writer is unable to give an adequate explanation of this fact, but it may have some bearing on the question whether potash is introduced or not in hydrothermal processes.

Group VIII: Sodium tetraborate solution upon feldspars and hornblende.—A few experiments were tried with borax solutions with results very similar to those produced by the alkali carbonates (Table VIII). In No. 43 well-formed crystals of analcite as rhom-

TABLE VIII

No.	Mineral	Time	Solution	Concentration	Vol. Sol.	Vol. Tube	Temp.	Press. Atm.	Results
43..	Adularia	15 days	Na$_2$B$_4$O$_7$	N/4	50 c.c.	100 c.c.	233° C.	30	Analcite
44..	Albite	15	"	"	50	95	233°	30	No change
45..	Hornblende	15	"	"	50	90	233°	30	" "

bic dodecahedra appeared. No alterations occurred in the other experiments.

Group IX: Sodium sulphide solutions upon feldspars and hornblende.—The presence of the metallic sulphides indicates that at

certain phases of the vein-forming process sulphide solutions must be present.„ Though the solutions are undoubtedly very complex, their efficiency as hydrothermal agents is very probably due to a few components. The physical state of these solutions has been recently shown by Tolman and Clark[1] to depend decidedly upon the composition, at least at ordinary temperatures, and it may also have some decided influence upon the character of the alteration. In the following experiments the copper tubes were vigorously attacked and chalcocite crystals lined the walls of the tubes (Table IX). In No. 46 needles of the anisotropic crystals like those

TABLE IX

No.	Mineral	Time	Solution	Concentration	Vol. Sol.	Vol. Tube	Temp.	Press. Atm.	Results
46..	Adularia	15 days	Na_2S	$N/2$	50 c.c.	120 c.c.	233° C.	30	Analcite and needles
47..	Albite	15	"	"	50	100	233°	30	Analcite
48..	Hornblende	15	"	"	50	105	233°	30	No change

obtained in experiments Nos. 25 and 34 were formed, together with well-formed analcite crystals. Very little of the original feldspar remained. In No. 47 perfect analcite crystals appeared as icosite-trahedra and as combinations of the cube and rhombic dodeca-hedron. These vary in size from one-half to one millimeter in diameter. The hornblende in experiment No. 48 was not attacked and no pyrite could be identified in the product. No sulphur was obtained by heating the mass in a closed tube. The results with the feldspars are quantitatively greater than in any other experiment; this was probably due to the fact that the hydrogen sulphide is a weaker acid than is carbonic acid and the hydrolysis therefore produces a more strongly alkaline solution.

Group X: Aluminate solutions on feldspars and hornblende.—In the previous experiments the loss of silica from the minerals resulted in an apparent rise of the alumina content of the new minerals. With the thought that possibly an increase in the concentration of the alumina in the solutions might cause the solubility product for

[1] C. F. Tolman and J. D. Clark, *Econ. Geol.*, IX (1914), 559.

compounds richer in alumina to be exceeded, a few experiments with aluminate solutions were tried. These solutions were prepared by taking a weighed quantity of aluminum sulphate, precipitating the aluminum as hydroxide, washing the precipitate and then adding it to normal sodium or potassium hydroxide and diluting

TABLE X

No.	Mineral	Time	Solution	Concentration of K or Ka	Vol. Sol.	Vol. Tube	Temp.	Press. Atm.	Results
49..	Adularia	15 days	Sodium aluminate	N/2	40c.c.	80c.c.	280° C.	65	Analcite
50..	"	15	Potassium aluminate	"	40	85	280°	65	Hexagonal plates and needles
51..	Orthoclase	15	Potassium aluminate	"	60	120	280°	65	Hexagonal plates and needles
52..	Albite	15	Potassium aluminate	"	30	70	280°	65	Hexagonal plates
53..	Hornblende	15	Potassium aluminate	"	35	75	280°	65	No change

one-half. After this had been allowed to stand for several hours it was filtered from its slight precipitate (Table X). In No. 49 analcite crystals formed, which were identified chemically and microscopically. In Nos. 50, 51, and 52 twinned hexagonal plates, with anomalous division into fields under polarized light, resulted, as shown in Fig. 8. These gelatinize with hydrochloric acid and contain sodium, but no aluminum could be detected in them by a microchemical test. The hornblende was not attacked.
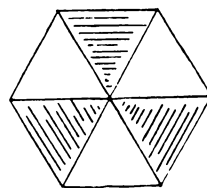

FIG. 8.—Twinned hexagonal plate resulting from experiments Nos. 50, 51, and 52.

Group XI.—Albite and hornblende were heated for 15 days at 280° C., with saturated solutions of calcium bicarbonate. The tubes burst in each case and the minerals showed no change.

GEOLOGIC BEARING

Though the alteration of feldspars to analcite has not been commonly described, in many cases it is very possible that some of the

determinations of isotropic minerals as glass may be incorrect, and that analcite has been overlooked.   In examining the slides in the University of Chicago collection a slide from a trachyte of Bannber-scheid, Westerwald, Nassau, was found which showed the soda feldspars altered to analcite though the original crystal boundaries remained sharp.   The alteration does not follow cleavage cracks but appears in irregular patches.   Mr. K. F. Mather in a forth-coming paper will describe an eruptive cone of Quaternary age in the canyon of the Mancos River ten miles southwest of Mancos, Colorado—locally known as the "blowout"—which is cut by dikes of augite minette.   These dikes carry fragments of granite xenoliths which are deeply corroded and partially assimilated.   The feldspars are altered to analcite—identified microchemically.   A careful study of rock specimens would probably show that this type of alteration is much more common than has been supposed.

SUMMARY

1. Alkaline solutions of different characters dissolve the feld-spars with separation of silica and crystallization of compounds less rich in silica.   The solutions are probably hydrolyzed since the reactions are accelerated by the presence of alkalies, by increased concentration of the alkalies, and by higher temperatures.

2. Feldspars and hornblende are not appreciably attacked by pure water at temperatures up to about 300° C. adularia to at least 350° C., showing that the dissolved substances rather than water alone must cause the differences in the nature of the alterations.

3. Albite and orthoclase feldspar seem to respond to the action of the alkalies in nearly identical ways, and hence the conclusion is patent that they have very similar chemical structures.

4. The influence of small amounts of fluoride and borates as mineralyzers has not been found important, at least in the presence of the other substances.   This leads to the suggestion that possibly the mineralyzing effect is merely that of causing solution at tem-peratures where the silicates in question would otherwise be much less soluble.

5. It is notable that no kaolin or kaolin-like substance forms from alkaline solutions at temperatures up to 280° C.   The sugges-

tion seems necessary that since pure water has practically no effect on the feldspars, and that since the alkaline waters produce minerals other than kaolin, kaolin probably forms by the action of acid solutions upon the feldspars. The literature bearing on the field occurrences of kaolin shows a striking lack of references to association of carbonates and kaolin, though this would be expected if carbonated waters are the cause of the formation of kaolin from the feldspars.

6. The general agreement of the data obtained throughout the range of temperatures used shows that the silicates may be studied with the apparatus described, up to 300° C., with gratifying results and without great mechanical difficulties, and also without the necessity of contamination from undesirable sources such as glass tubes.

The writer is indebted to Professor W. H. Emmons for suggesting the problem and to Professor A. D. Brokaw for sincere interest and many suggestions during the progress of the work. Further work of a similar sort is in progress and the next paper will deal with the action of various acid solutions, especially hydrofluoric acid on the same group of minerals.